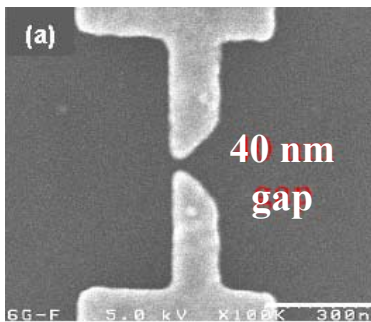
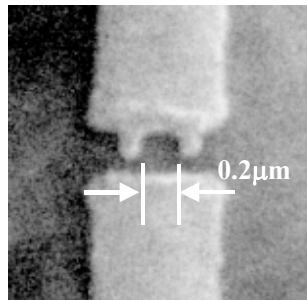


# Challenges in Nanoscale Materials Synthesis, Integration and Applications

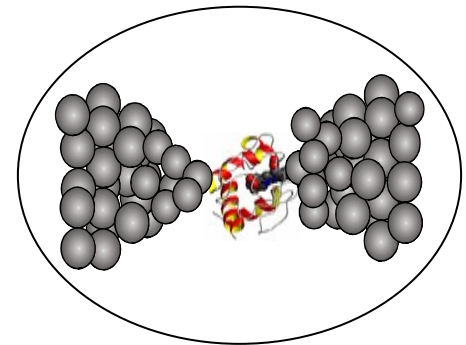
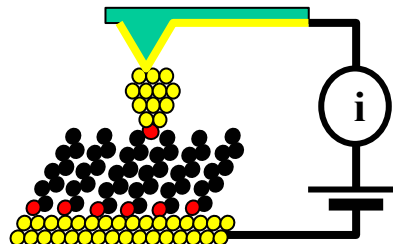
S. Tom Picraux  
Arizona State University  
Tempe, AZ



Single electron transistor



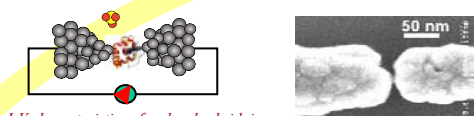
Single molecule transport



# Examples of challenging areas of integration

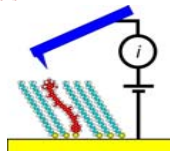
## Molecular Sensors

### Molecule Electronic Sensing

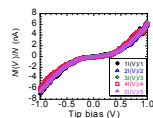


*I-V characteristics of molecules bridging nano-gap for novel chemical/biological sensors*

*Electroplated nano-gap between metallic electrodes.*



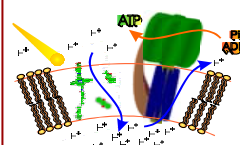
*Conducting tip AFM used to measure electrical characteristics of single molecules*



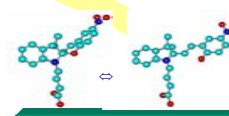
*Devices give universal current-voltage data, quantized in steps reflecting the number of molecules in the junction.*

## Hybrid Biodevices

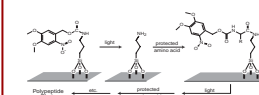
### Organic and Interfacial Chemistry



*Nanoscale biological power plant*



*Spiropyran attached to an oxidized silicon surface undergoes a Zwitterionic transformation after exposure to u.v. light*



*The chemistry used for photochemically coupling molecules to glass*



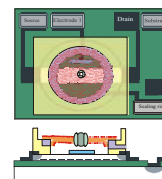
*Structure of a single zinc finger from the Dsnr Zinc Finger Peptide (PDB 1A1F).*

## Nanomanufacturing

### Nanofluidics/Nanoimprint



*Integrated DNA Lab-on-a-Chip*



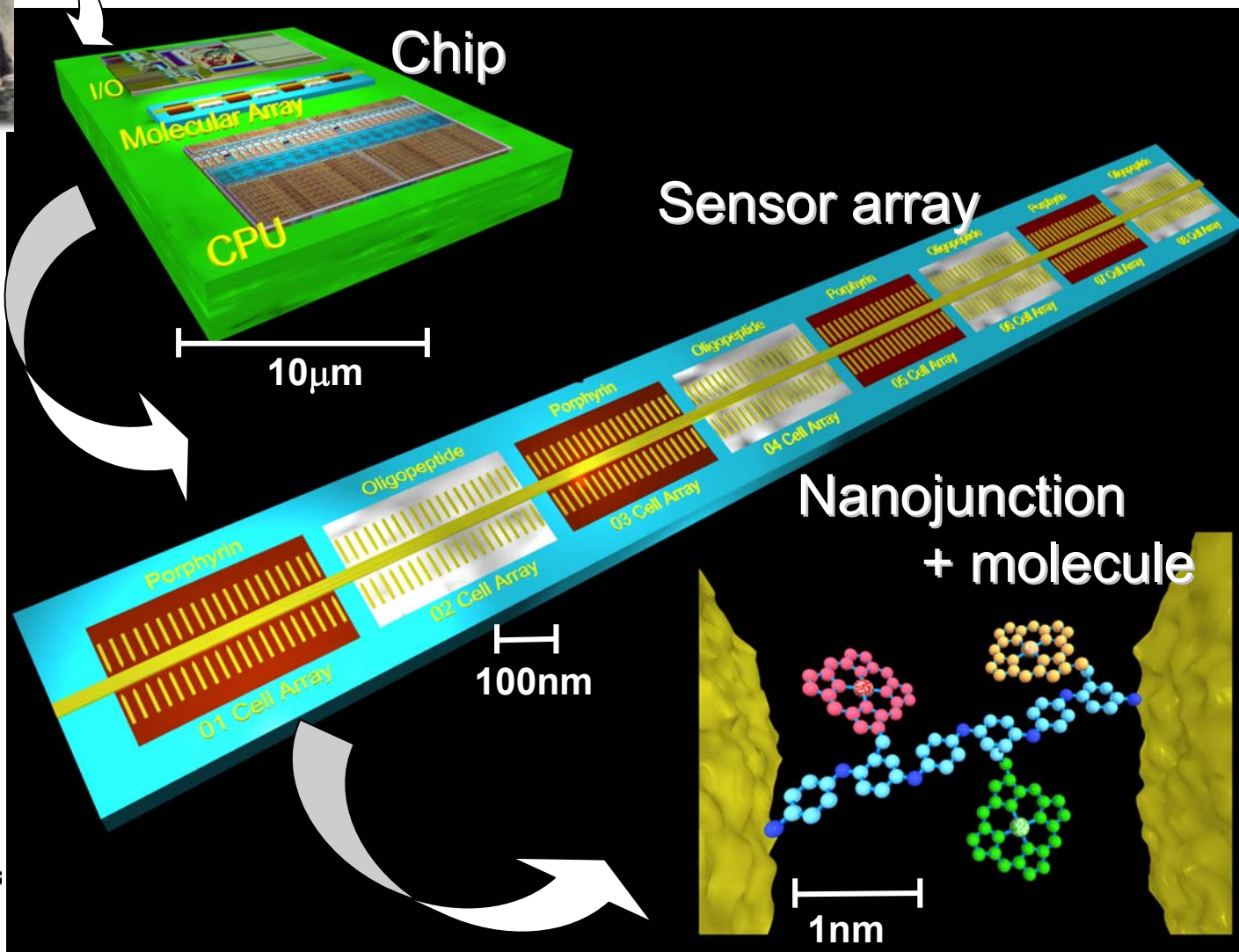
*Plan view and cross-section of an integrated ion-channel sensor.*



*PMMA fluidic network and the laser-scanner acquired image of Cy-3 labeled oligonucleotides spotted into the biochannels of the fluidic network.*

# Nanojunction Molecular Sensing

## *The approach*



Sandia  
National  
Laboratories



MOTOROLA

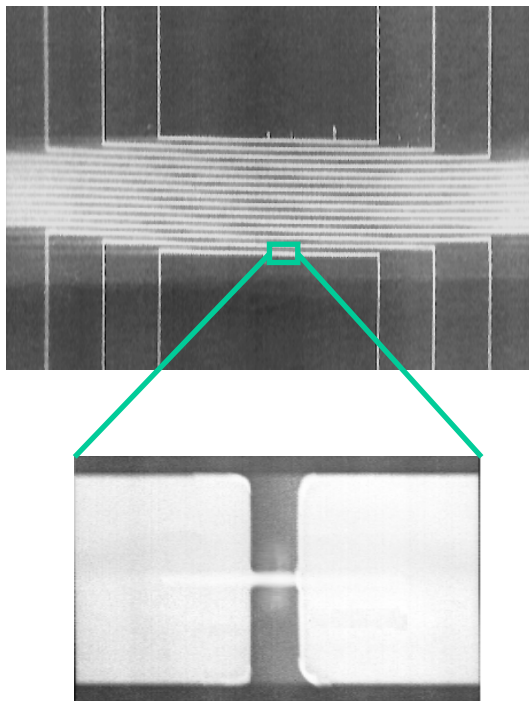
# Fabricating Molecular Scale Nanojunctions

**Top down nanoelectrode definition to 40 nm.**

**Self limiting electrochemical deposition to 4 nm.**

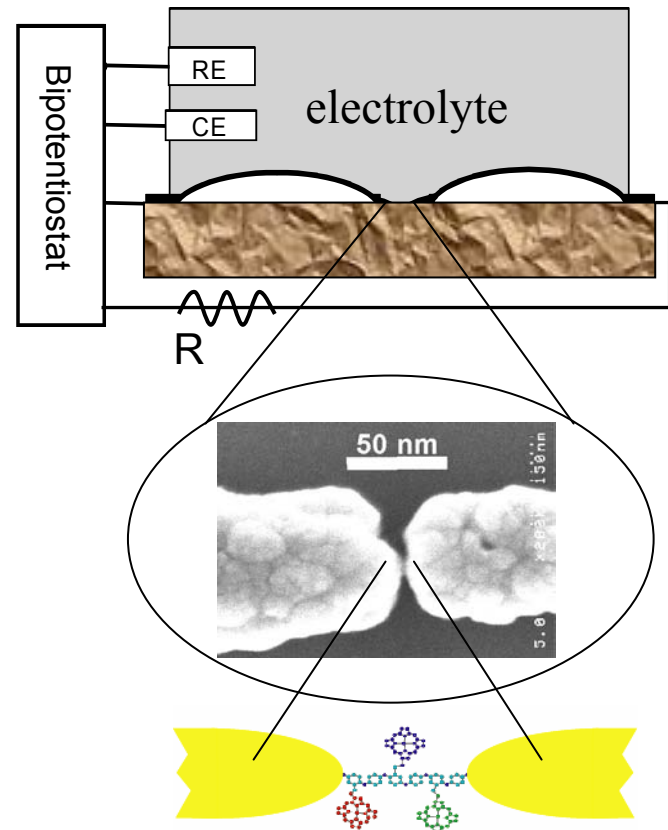
**Self assemble molecular wires & functionalize.**

Deep UV lithography



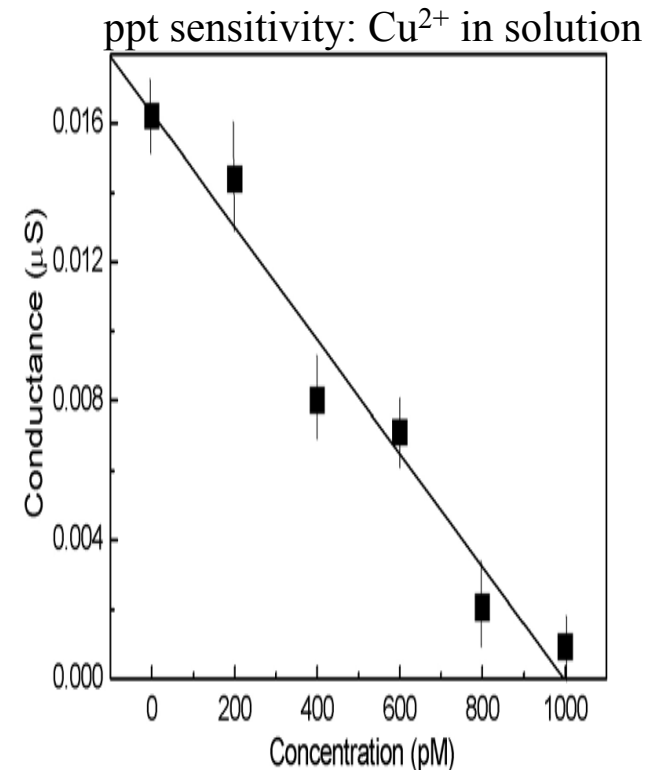
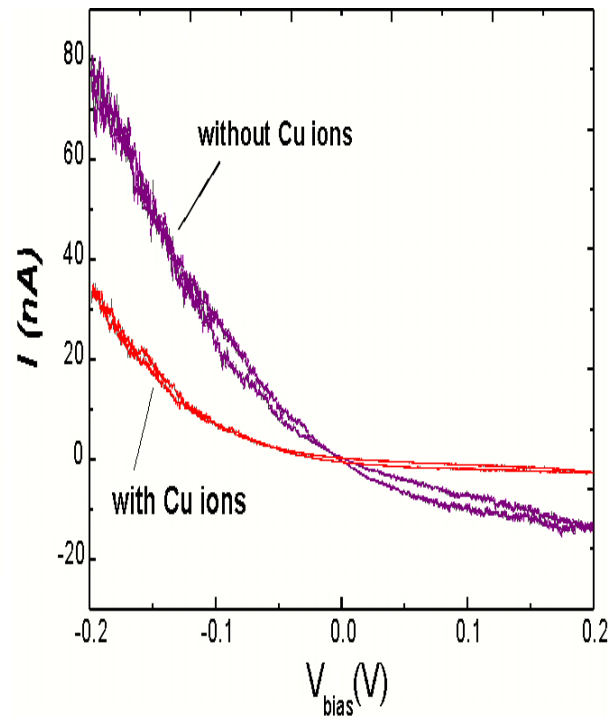
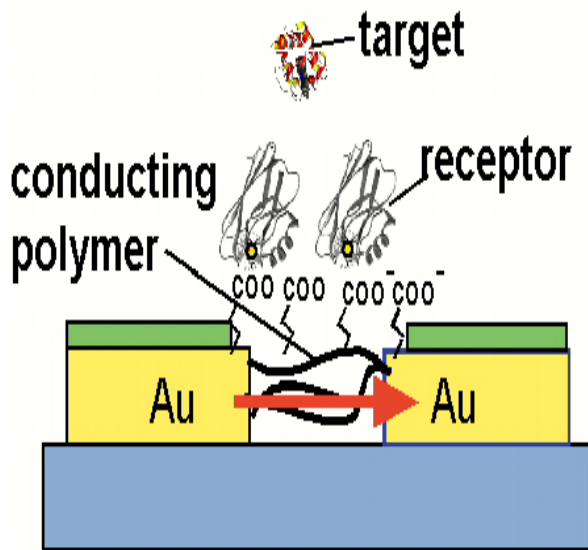
Tao, ASU w/Motorola

Electrochemical deposition



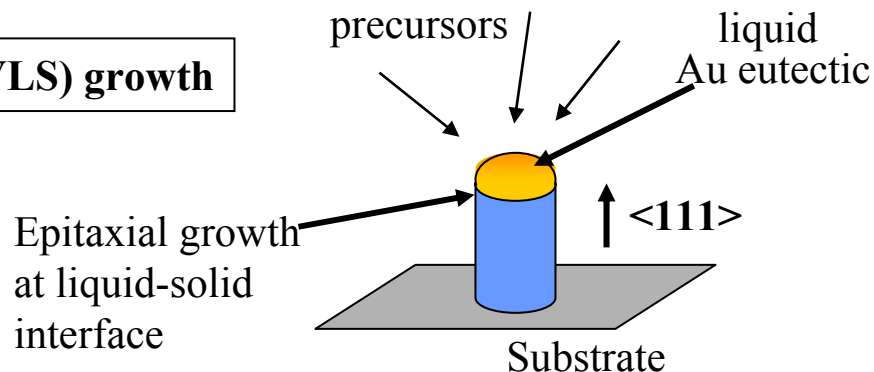
# Nanojunction Sensing with Polymer Nanowires

## Au-polyaniline-Au nanojunction with Gly-Gly-His oligopeptide for sensing $\text{Cu}^{2+}$



# Integration of Nanostructures: Nanowires

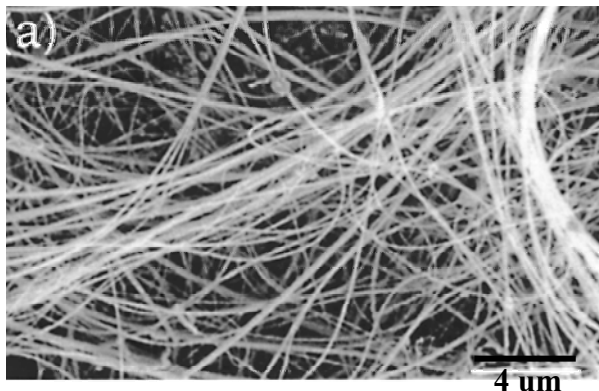
## Vapor Liquid Solid (VLS) growth



## Unseeded semiconductor nanowires

(various materials, much Si, few Ge)

**Ge, sealed tube vapor transport, Au catalyzed**

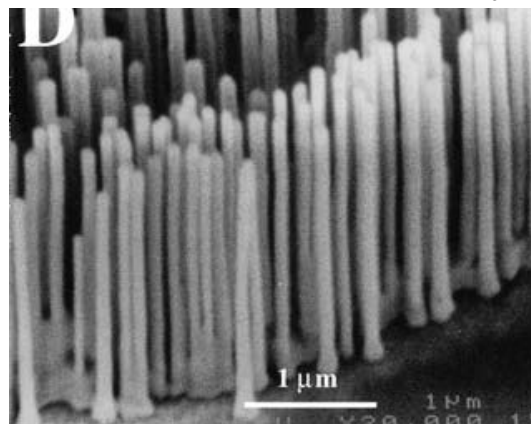


Y. Wu & P. Yang, Chem. Mater. 12, 605 (2000)

## Nano-heteroepitaxy

(mostly III-V, II-VI)

**ZnO nanowires, Au catalyzed**

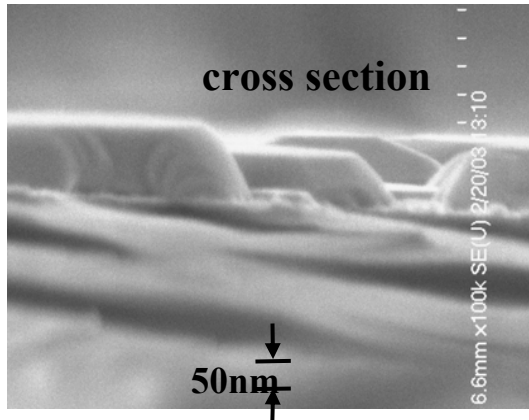


M. Huang et al., Science 292, 1897 (2001)

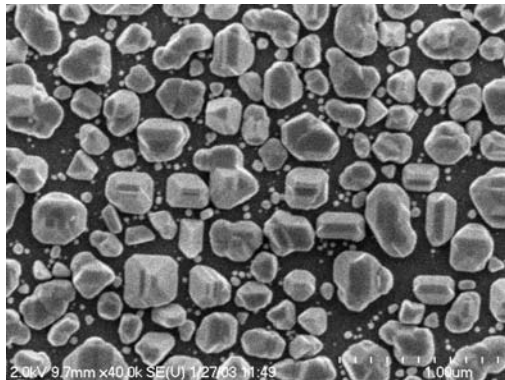
# How do we integrate synthesis with device platforms

## VLS Ge nanopillars and nanowires on Si

Lower pressures—gas phase MBE nanopillars



Si (111) substrate, 580°C

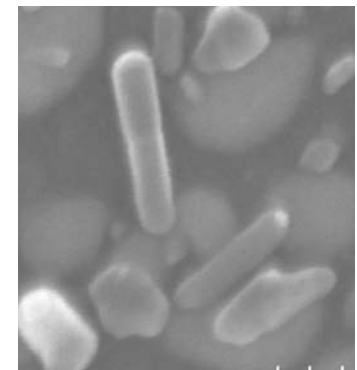


Si (100) 600C

## Heteroepitaxial growth of 1-D structures on Si

- Large lattice mismatch
- Low defects
- Quantum structures and arrays
- Nanowire sensors, photonic lattices, ...

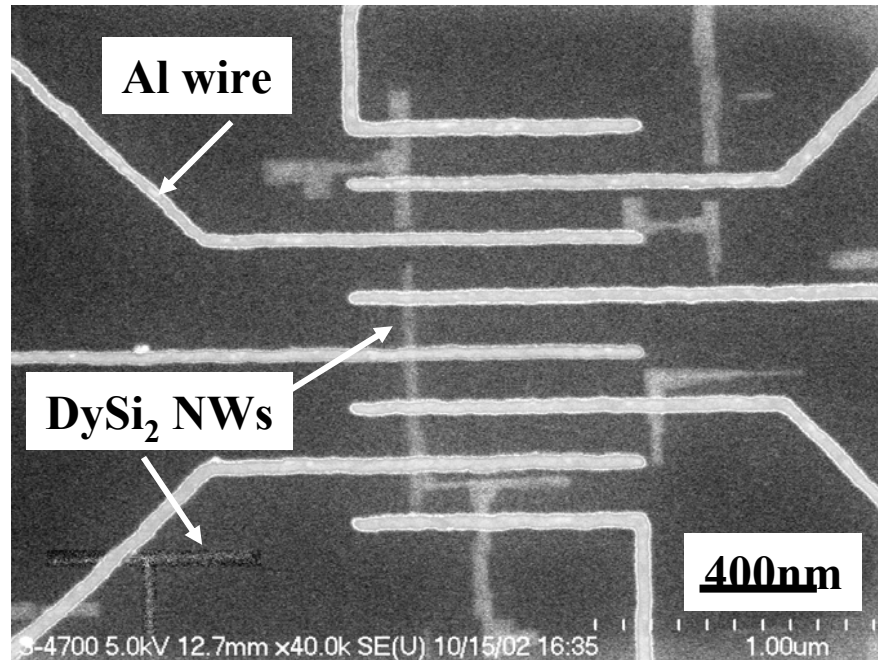
Higher pressures—transition to nanowires  
2  $\mu\text{m}$  length, highly catalytic  $\Rightarrow \alpha \sim 0.5$



Si (111) 400C

# Integration of Silicide Nanowires on Si

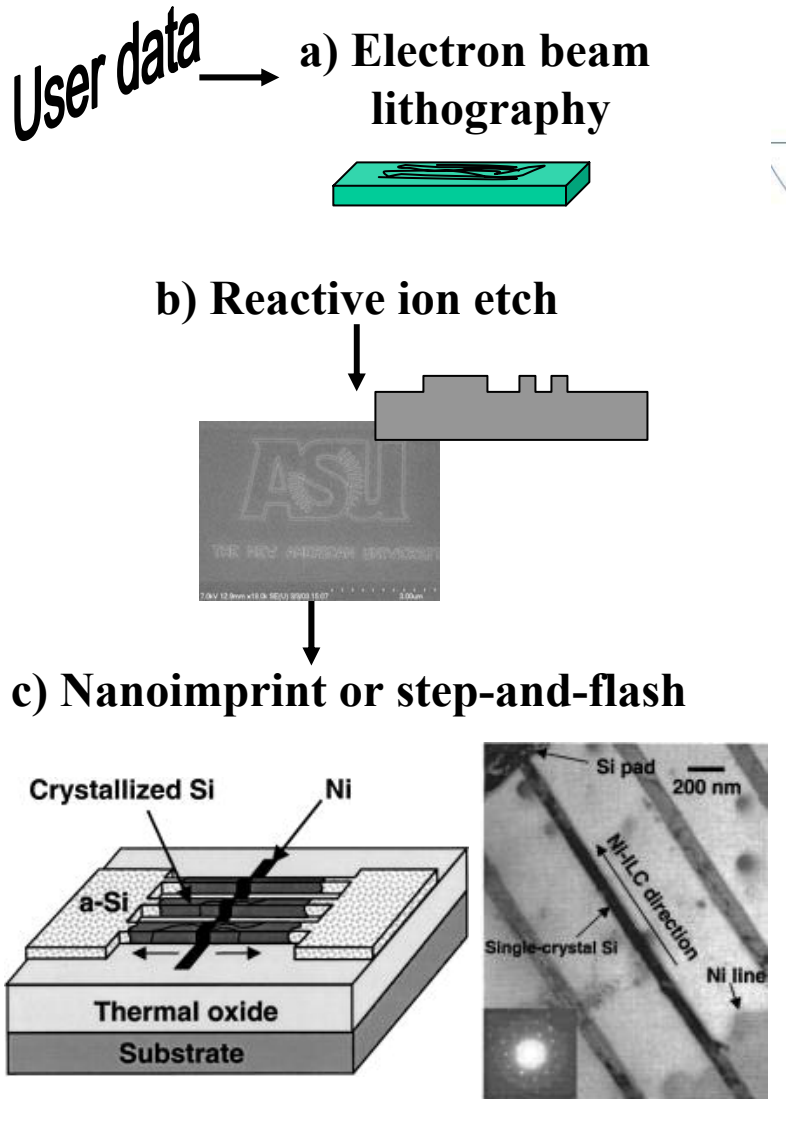
Silicide Nanowires for Nanoelectronics  
NIRT, 2003



DySi<sub>2</sub> nanowires with EBL-defined contacts  
(Jie-Feng Lin, J. Bird, P. Bennett – ASU)

# Novel approaches to nanofabrication

## Nano-imprinting/step-and-flash



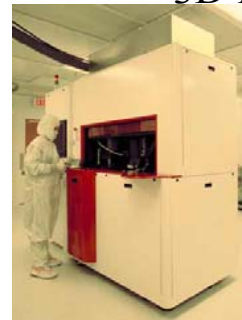
STS ICP Etcher



Nanonex NX1000  
10nm features  
High Throughput (<1min)  
3D features

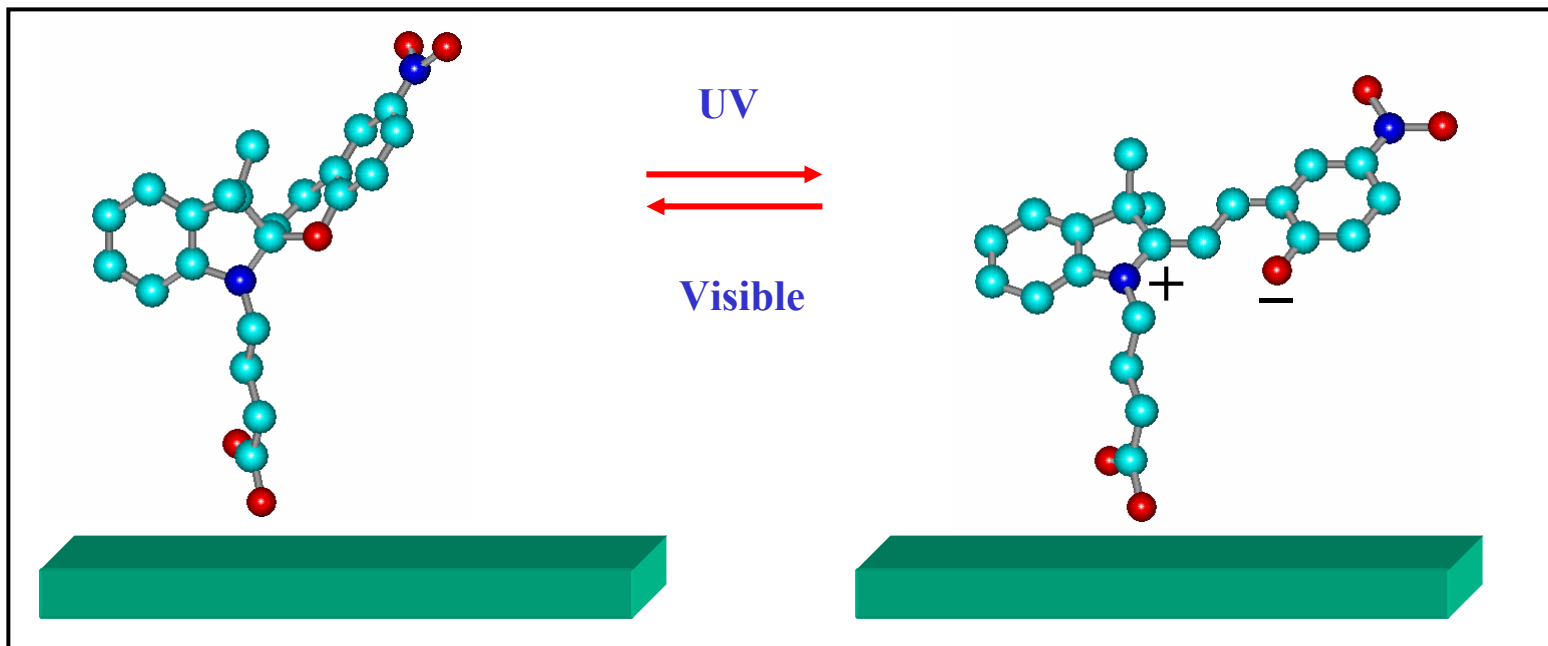


Molecular Imprints S-FIL  
Sub-100 nm resolution  
8" wafer capability  
Step and repeat process

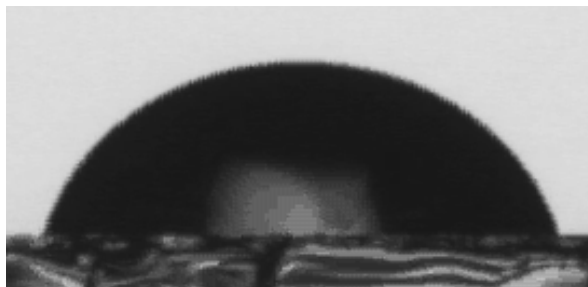


# Integration of Nano-bio Structures onto Surfaces

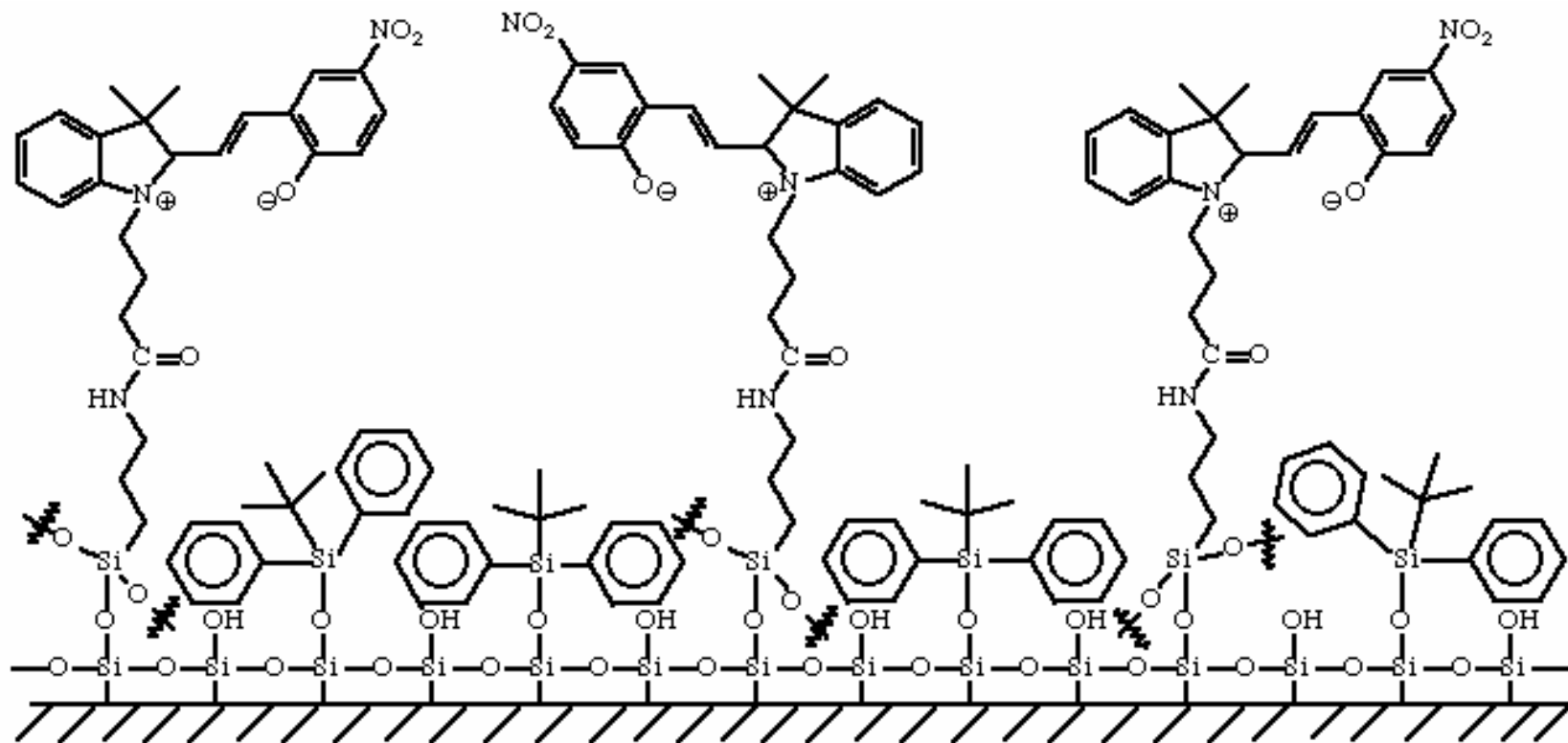
## Photoactive Spiropyran Influences Charge, Polarity of Surface



*Designer surfaces—photoswitchable hydrophobicity*

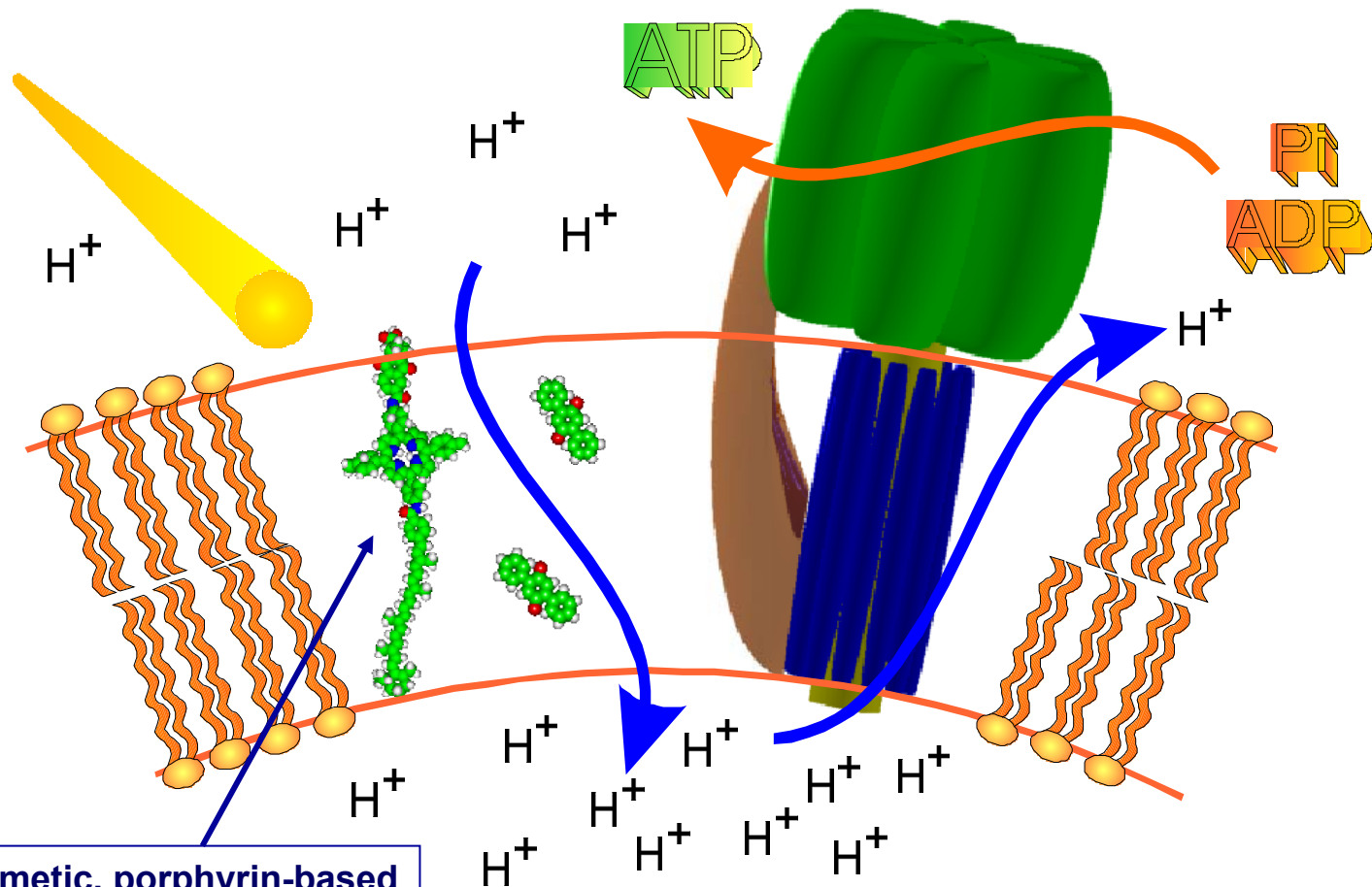


# Design of Tethered Spiropyran Surfaces



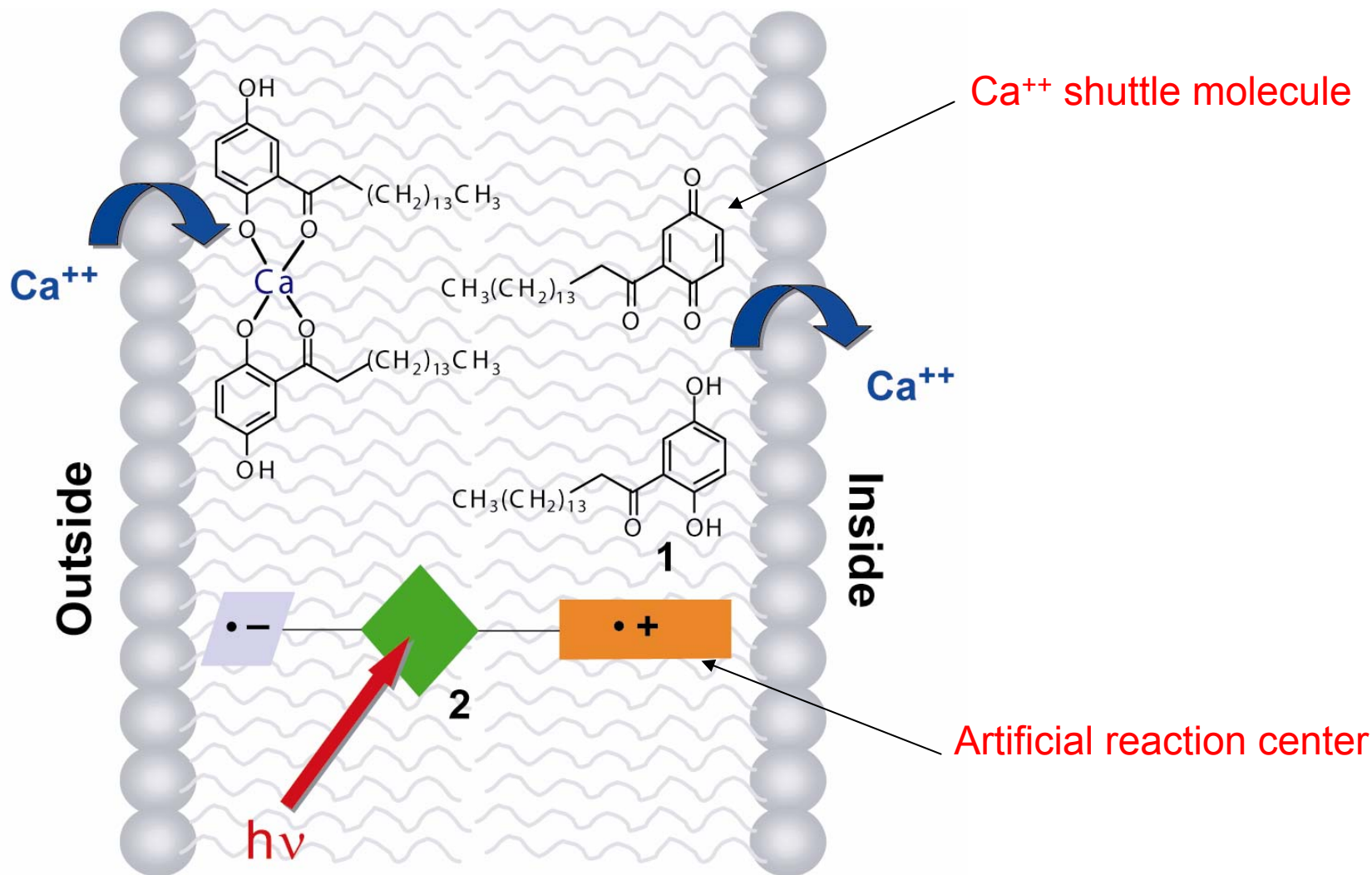
- Short-chain amine provides covalent amide link to spiropyran
- Tert-butyl biphenyl groups provide spaces to promote photo-reversibility.

# Artificial Biological Power Plant



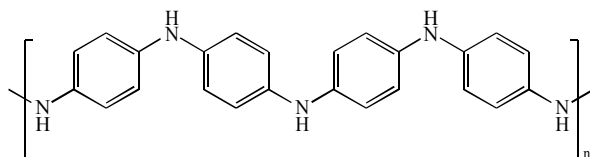
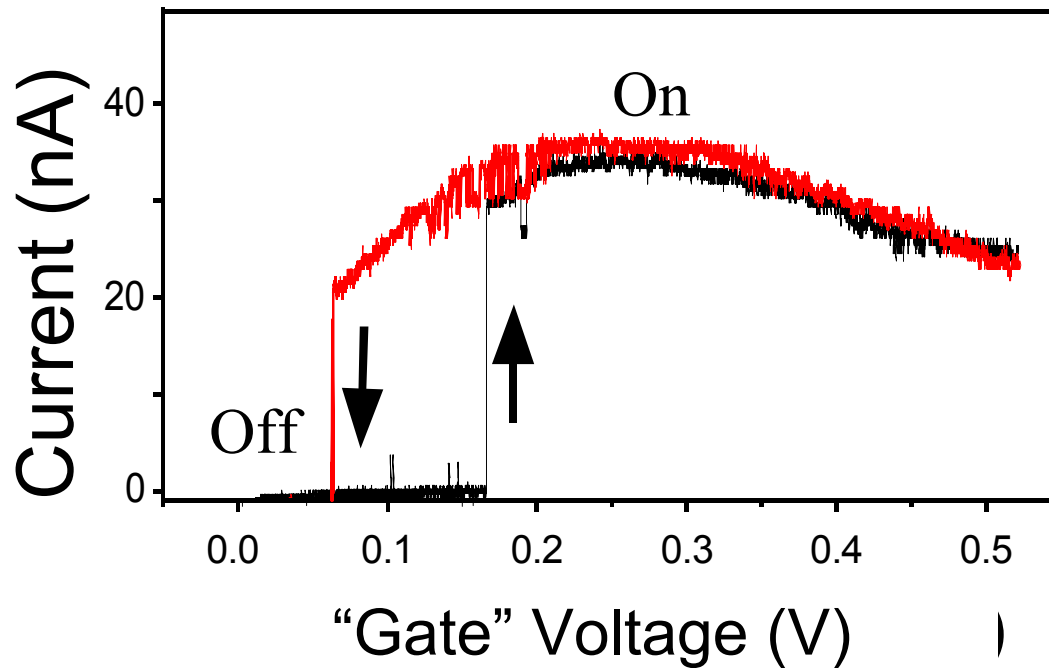
Biomimetic, porphyrin-based  
"triad" single-molecule  
photovoltaics

# Integration of Soft-Hard Systems: Light-Powered Calcium Ion Pump

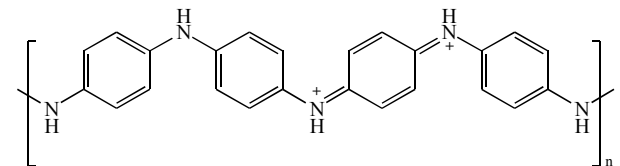
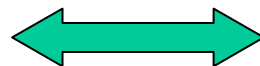


Backup

# A Polyaniline Switch

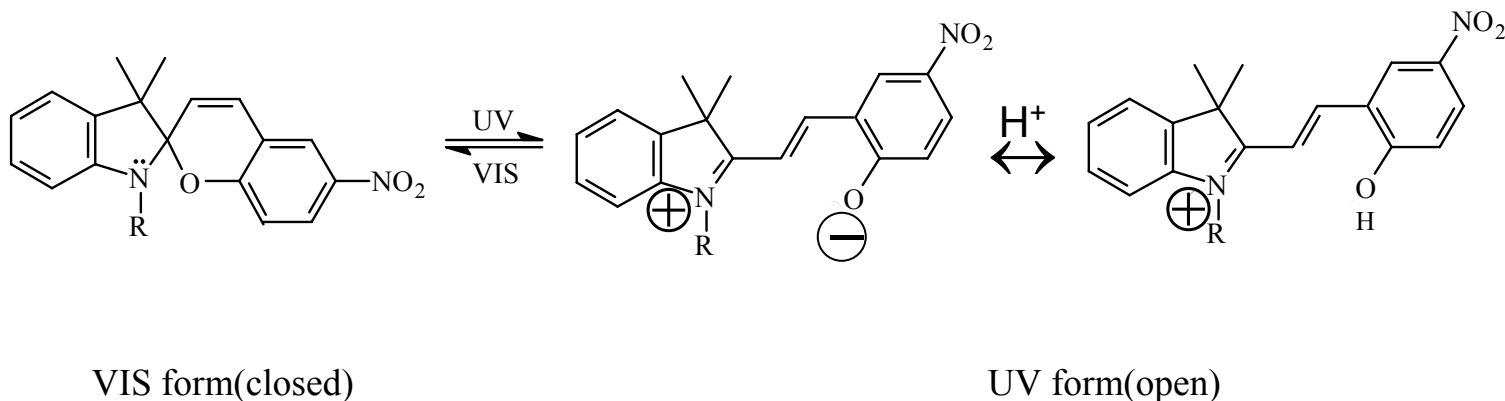


Off: Insulator



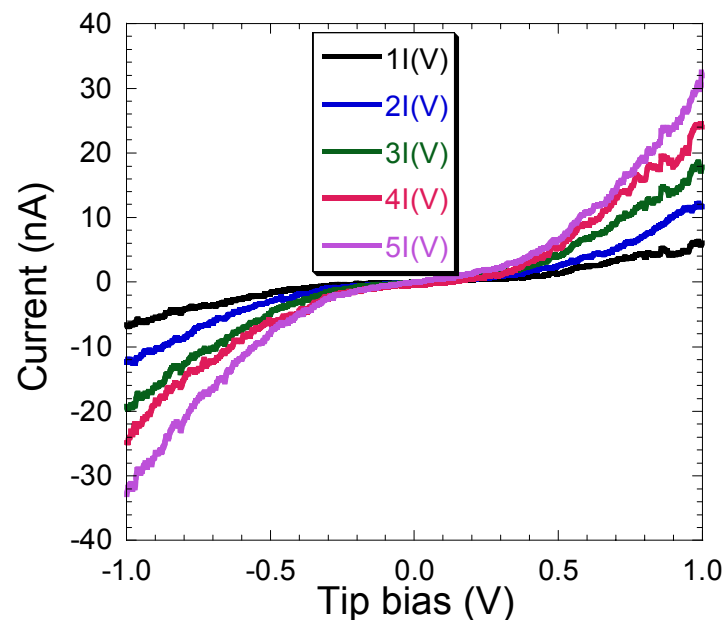
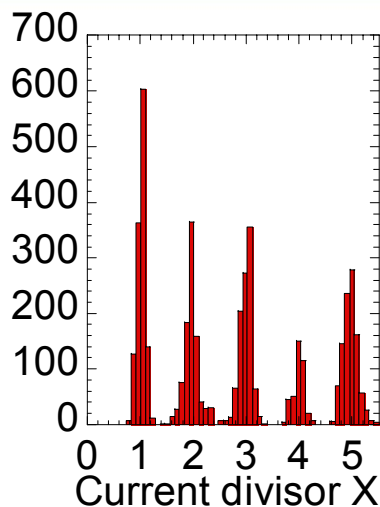
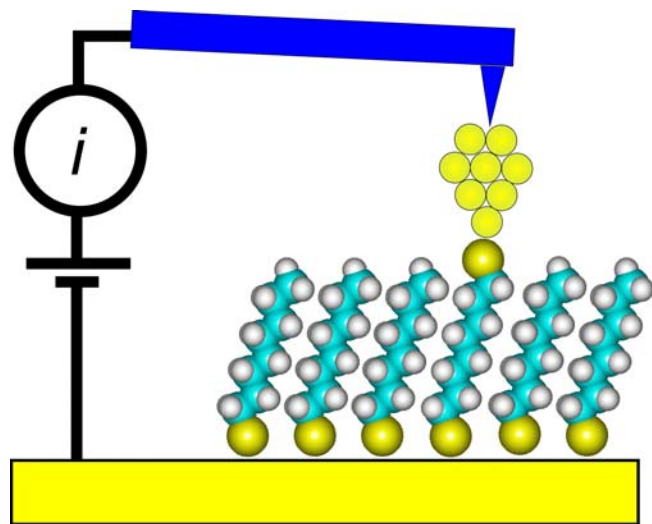
On: Conductor

# Conclusions : Switching in Tethered Spiropyrans



- 1) UV and visible lights open and close rings in tethered spiropyran.
- 2) In air, ring opening creates a more polar surface, with surface dipoles pointing toward the surface.
- 3) In water, ring opening creates positive surface sites due to protonation of phenoxide group in the open ring.
- 4) Switching of spiropyran provides a mechanism for manipulating double layer forces in microfluidic systems.

# Measuring Single Molecule Conductivity



Resistance of 1 molecule = 900 megohms  
Resistance of nonbonded contact  $>9 \times 10^6$  megohms

X. D. Cui, A. Primak, X. Zarate, J. Tomfohr, O. F. Sankey, A. L. Moore, T. A. Moore, D. Gust, G. Harris, S. M. Lindsay

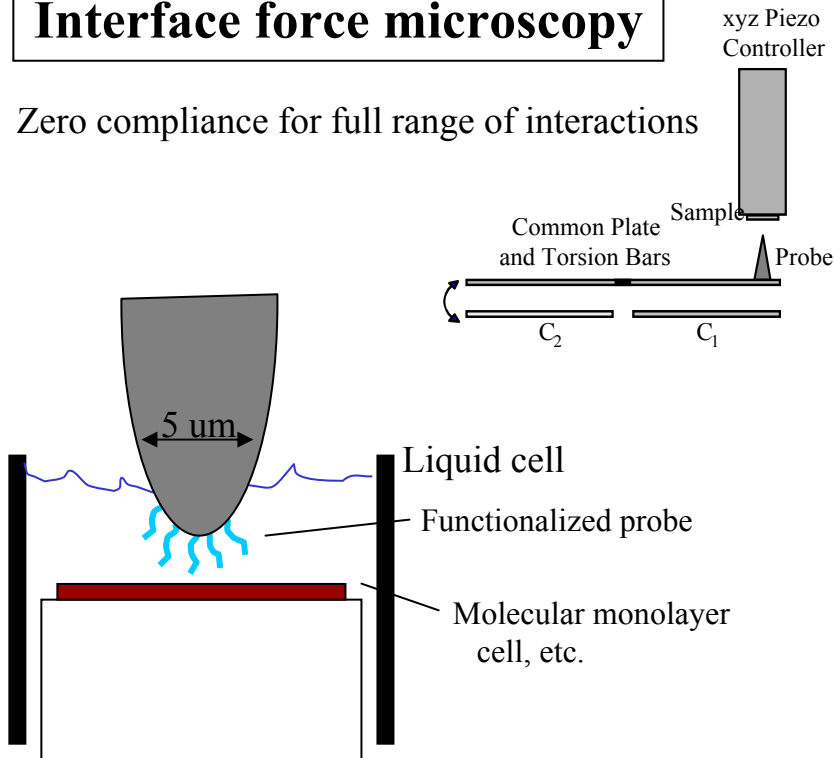
*Science* **2001**, 294, 571-574

# Probing (Bio)Molecular Interactions by Interface Force Microscopy

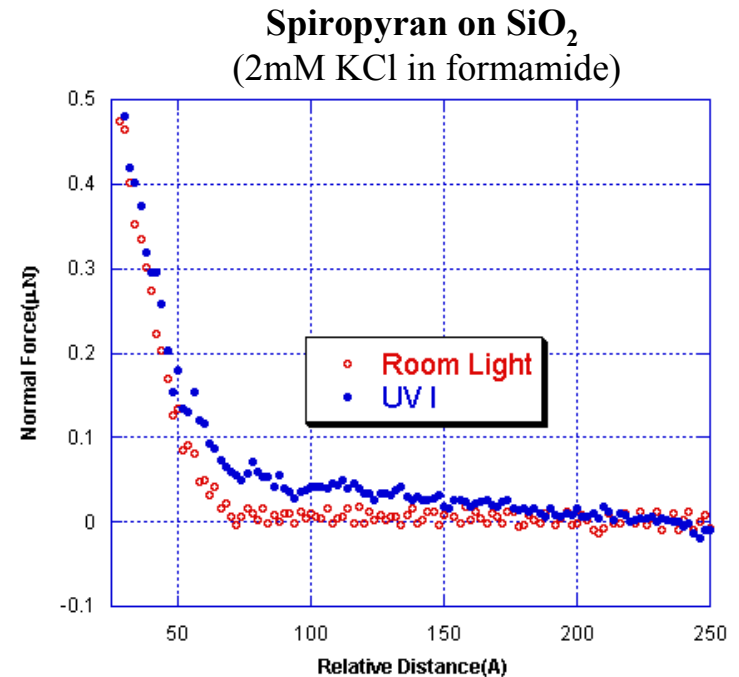


## Interface force microscopy

Zero compliance for full range of interactions



Example: Spiropyran surface  $\leftrightarrow$  silica probe in high dielectric liquid



*Nanoscale measurement of optical switching of molecular surface state*

Concept: Directly probe (bio)molecular interactions between tip and surface